SOME SPECTRAL OBSERVATIONS ON TWO COKING LIGNITES

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INTRODUCTION

Berkowitz[1] and Berkowitz and Schein[2] first drew attention to the abnormal properties of a hard black lignite from the Sharigh region of Pakistan. These properties included a low heat of wetting of about 5 Cal./g. in methanol, a low inherent moisture content of 1.7%, and caking properties corresponding to a free swelling index of 5 to 5 1/2. Since these properties occurred in a coal with a carbon content of about 75% (daf) they were considered atypical and were attributed in part to unusual tectonic conditions occurring in the early stages of the formation of the coal. These were postulated to be of such a nature as to produce the low pore volume characteristic of the British medium volatile bituminous coals. Subsequently Kreulen[3] examined another lignite from Rasa in Istria (Yugoslavia), and noted a high swelling index of 9, a low inherent moisture content, and a high sulfur content of 11.0%, again with a low carbon content of 74.8%. Kreulen drew attention to the fact that if the carbon and sulfur contents are added together the result, about 86%, is equal to the carbon content of "normal" high swelling coals.

Both of these coals, together with a number of Alberta coals, have been examined in our laboratories by means of infrared spectroscopy and electron spin resonance techniques. In the case of the lignites another property of coking coals, the formation of chloroform-soluble material upon shock heating to about 400°C[4], has also been examined. Analyses of these coals on a dry-ash-free basis are presented in Table I.

RESULTS

Infrared spectra were prepared using the potassium-bromide pellet technique and the absorption patterns for the various coals are presented in Figure 1 for the long wavelength region. These spectra show that both the Rasa and the Sharigh lignites have the three characteristic bands[5,6] near 740, 810, and 870 cm.$^{-1}$ normally associated with coals with carbon contents of greater than 85%. Moreover, the pattern is stronger for the strongly swelling Rasa coal, FSI 9, than for the Sharigh coal, FSI 5.0 - 5.5.

These three bands have been associated with out-of-plane deformation vibrations of one, two, and four adjacent aromatic CH groups respectively[7]. The absence of these absorptions in normal lignites and subbituminous coals is an indication that in these materials the aromatic lamellae are heavily substituted and crosslinked. As a result, heating does not produce plasticity and related swelling. In bituminous coals the aromatic systems are less substituted and crosslinked as indicated by the presence of the three infrared absorption bands. Heating therefore results in the development of the plasticity behavior of coking coals. In the coking lignites the presence of these bands indicates that despite their low carbon content, the aromatic lamellae are sufficiently free of crosslinking to produce a product that is thermoplastic. In other words, the various ring systems can decompose in such a manner as to produce lamellae that, upon heating, can move about relative to each other. It should be noted that these bands are strong in anthracites as well but because of the growth of the lamellae[8] the attractive forces between lamellae are too strong to allow movement so that there is no thermoplasticity.

Closely related to the aromatic substitution pattern of bituminous coals as an indication of mobile lamellae is the development of considerable chloroform-soluble material upon shock heating these coals to the vicinity of 400°C. Again, the lack of crosslinking in the bituminous coal and the resultant need to break fewer bonds to produce thermoplastic polymers is indicated. Application of this test to the Sharigh and Rasa lignites produced the results shown in Figure 2. For comparison results are also shown for a subbituminous coal (Drumheller) and for a normal coking coal (Michel). It is readily seen that the coking lignites resemble the normal coking coal and not the subbituminous coal of comparable carbon content to the lignites. The peak in the plot of chloroform extractibles for the Rasa coal is much broader and occurs at a lower temperature than those of the other coals. It is apparent that the low molecular weight thermally produced material, which presumably acts as a plasticizing agent, produced in these lignites is similar to that from normal bituminous coal. This confirms the lack of crosslinking in these lignites in agreement with the infrared results.

The e.s.r. signals of the two lignites in question and of a number of Alberta coals were measured using a Varian Model 4500 electron paramagnetic resonance spectrometer fitted with 100 KC modulation. About 10 mg. of dry coal was placed in a glass tube and evacuated to 10^{-4} mm. for 1 hour. Measurement of the e.s.r. signals produced the results shown in Table II. The number of spins observed in the coking lignites is in the lower range observed for coals of comparable carbon contents[9] and much below that observed for normal coking coals. Accurate measurements of the g-values obtained by using a dual sample cavity showed that the three higher rank coals (Luscar, Michel, and Canmore) had g-values close to 2.0031 and the three lower rank coals (Wabamun, Drumheller, and Lethbridge) had g-values of 2.0036 to 2.0037. The coking lignites again resembled the low rank coals in having high g-values. The signals for the Pakistan lignite and two of the bituminous coals are distinctive in having dual peaks, Figure 3. The weak narrow signal is reversibly suppressed by the presence of oxygen. The g-values of the narrow signals in all cases was close to 2.0030 regardless of the position of the main signal. Since signals sensitive to oxygen are characteristic of material heated to temperatures in excess of 500°C these results suggest that charred material from local heating or very severe tectonic conditions might have been the source of the narrow signals.

DISCUSSION

The infrared spectra and shock heating experiments show quite definitely that the chemical structures of the coking lignites are responsible for the swelling properties of the two coals. Basically this is because the degree of crosslinking of the aromatic lamellae as indicated by the infrared absorption bands is quite low. Lack of polar functional groups accounts in part for the low moisture content and the so-called "liquid" structure and resulting low porosity accounts for the low heat of wetting.

The problem remains of deciding whether the lignites have these properties because of unusual starting material – both coals are high in sulfur – or because of unusual tectonic conditions or both.

The e.s.r. results which include low numbers of spins and high g-values are similar to the results for the low rank coals and in contrast to the results for the high rank coals. However, shifts in g-value of this magnitude result chiefly from atomic spin orbit coupling of atoms such as oxygen[10]. Thus the g-values of the coking lignites may be high simply because the free radicals are associated with moieties containing sulfur which cause an even larger g shift than oxygen atoms[11]. The narrow signal present in the Sharigh lignite may be indicative of severe tectonic conditions to which we know the Luscar and Michel coals were subjected.

The lack of substitution of the aromatic lamellae indicated by the infrared results suggests that breaking of weak sulfide bridges is not responsible for thermoplasticity. This is in agreement with the findings of Iyengar et.al.[12] who found no sulfide linkages in Sharigh lignite by oxidation studies. This indicates that sulfur seems to be to quite a large extent in the heterocyclic aromatic donor or quinonoid acceptor structures the interaction of which is responsible for the free radical signals[13]. This suggestion is in agreement with the finding of Kavcic of 70% of the S in Rasa coal occurring in ring structures[14].

The low number of spins in the coking lignites compared with normal bituminous coals may be a result of the sulfur content. That is sulfur may be a poorer donor compared to carbon or a weaker acceptor compared to oxygen and charge transfer complexes are as a result weaker. This point is supported by the light color of the Rasa coal.

On balance the infrared and e.s.r. evidence suggests that these lignites were subjected to fairly severe tectonic conditions. Because of the unusual constitution of the starting material, a low carbon content resulted but with the aromatic structures resembling a normal bituminous coal as revealed by the infrared evidence.

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TABLE I

Analyses of Coals

Coal	% - d.a.f.			
	C	H	N	S
Rasa	75.0	5.71	1.7	11.22
Sharigh	75.80	6.08	1.7	4.15
Wabamun	75.9	4.7	-	0.1
Drumheller	75.9	5.1	2.0	0.6
Lethbridge	79.7	5.6	2.5	0.9
Michel	89.1	5.2	1.4	0.4
Luscar	90.6	5.0	1.3	0.2
Canmore	91.5	4.4	1.9	0.6

TABLE II

E.S.R. Spectra of Coals

Coal	g-value (in vacuo)	spins/g. (in vacuo)	width (oersted)
Rasa	2.00395	3.8×10^{18}	6.9
Sharigh	2.00381 Broad	4.3×10^{18}	7.9
	2.00288 Narrow	4×10^{16}	1.0
Wabamun	2.00372	1.1×10^{19}	7.1
Drumheller	2.00360	7.5×10^{18}	6.3
Lethbridge	2.00370	1.8×10^{19}	7.5
Michel	2.00304 Broad	1.5×10^{19}	6.5
	2.00285 Narrow	2.2×10^{17}	0.8
Luscar	2.00310 Broad	1.1×10^{19}	4.7
	2.00310 Narrow	2.4×10^{17}	0.5
Canmore	2.00317	1.6×10^{19}	4.7

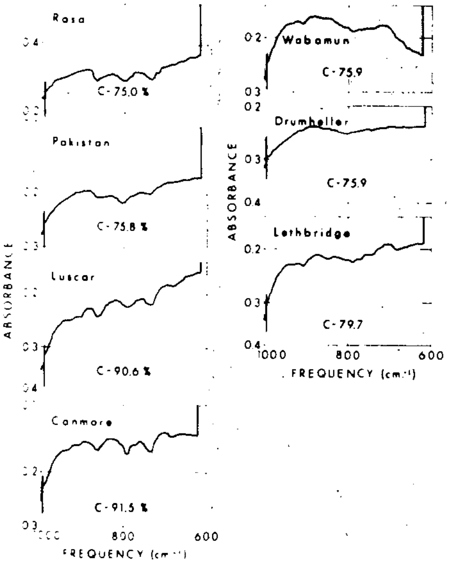

Fig. 1. Infrared spectra of coals in the region of 1000 - 600 cm.$^{-1}$ (0.2% in KBr).

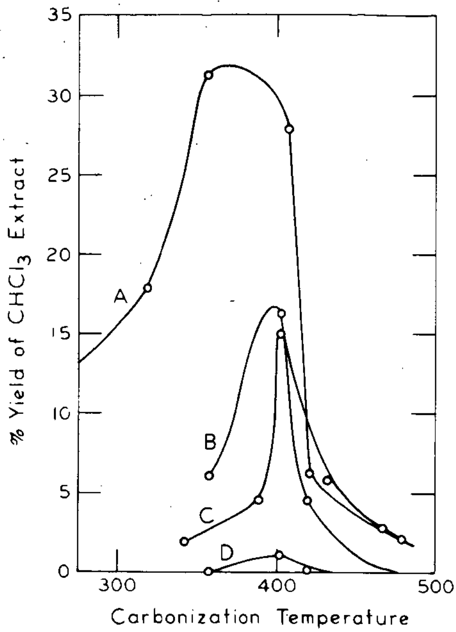

Fig. 2. Yield of chloroform - soluble material as a function of temperature of shock heating of coal.
(A) Rasa; (B) Sharigh; (C) Michel, B.C.; (D) Drumheller, Alberta.

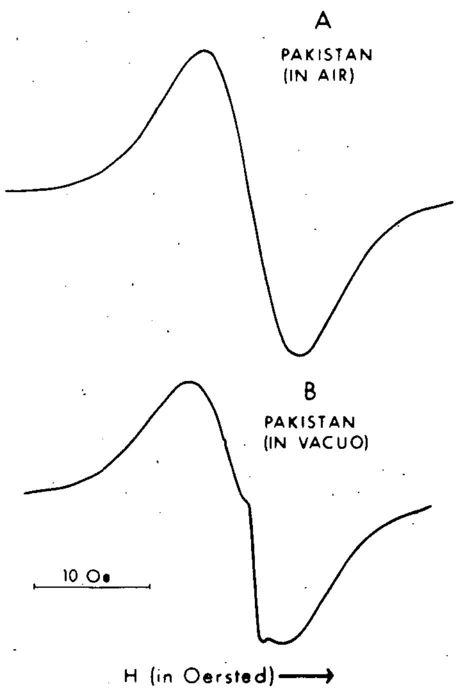

Fig. 3. Electron spin resonance spectra of Sharigh lignite.
(A) spectrum from the sample in air;
(B) spectrum from the sample in vacuo.